

consequence. The intensity had diminished, however, by nearly 25 per cent.

Similarly the magnet which had been given a negligible coefficient by cutting the length of the wire to 8 cm., as cited above (p. 219), after being boiled at intervals for four hours, was found five months later to have changed so little that its coefficient might still be considered negligible.

Further experiments, however, upon this question and some others arising out of this investigation are now in progress.

“The Electric Conductivity of Nitric Acid.” By V. H. VELEY, M.A., F.R.S., and J. J. MANLEY, Daubeny Curator of the Magdalen College Laboratory, Oxford. Received November 1,—Read December 9, 1897.

(Abstract.)

In this paper an account is given of determinations of the electric conductivity of nitric acid of percentage concentrations varying from 1·3 to 99·97, purified, so far as possible, from reduction products of the acid, as also from sulphuric and the halogen acids, with which it is likely to be contaminated from its process of manufacture. In the preliminary experiments it was observed that the results might be vitiated by (i) a trace of nitrous acid either directly added or produced by decomposition due to exposure to sunlight, and (ii) imperfect insulation of the electrolytic cell caused by metallic clamps, a point which seems to have been neglected by previous observers.

The methods adopted for the purification of the water and nitric acid, as also for the detection and estimation of the impurities, are described in full. The greatest quantity of nitrous acid, sulphuric acid, and the halogen acids found in any sample used were 0·75, 4·3, and 3·8 parts per million respectively.

The thermometers, resistance coils, and other instruments used were compared with certain standards and corrected accordingly; the burettes and electrolytic cells were calibrated by one or more methods, and the mean of the values accepted.

The method adopted for the determinations was in outline that originally described by Kohlrausch, but modified so as to overcome certain difficulties experienced. A particular form of bridge was constructed, in which the wire was an air line, and a special form of slider adopted to tap without sagging the wire, so arranged that it could be moved by the observer from the extremity of the bridge, and thus all thermo-currents due to his proximity were avoided.

A rapidly revolving commutator was substituted for the usual induction coil, as the latter was found to be unsatisfactory owing to the susceptibility of nitric acid to polarisation.

Various forms of electrolytic cells were used according to the concentration of the acid and the temperature of the observations; these were provided with movable electrodes, so as to throw into circuit different lengths of acid.

A special form of apparatus was devised to prepare nitric acid of 99.88 per cent., and another form to obtain acid of 99.97 per cent. from the latter. As a considerable quantity of this practically anhydrous acid was obtained, its chemical and certain physical properties were examined. It has no action on (i) copper, (ii) silver, (iii) cadmium, and (iv) mercury, all of high degree of purity, and (v) commercial magnesium, at ordinary temperatures; purified iron and commercial granulated tin were unaffected by the acid, even when boiling. Purified zinc was slightly acted upon, but sodium immediately caught fire. The acid has no action whatever on calcium carbonate at ordinary temperatures or the boiling point. Flowers of sulphur and iron pyrites dissolve quickly and completely in the gently warmed acid. The following results were obtained for the density of the 99.97 per cent. acid, corrected for weighings *in vacuo*:—

$$\text{Density } 4/4 = 1.54212; 14.2/4 = 1.52234; 24.2/4 = 1.50394,$$

the mean values of two concordant observations.

As a further check upon the measurements obtained by the Kohlrausch method, certain other measurements were made by Carey Foster's method for the comparison of resistances, and the results obtained were found to be concordant within the limits of experimental error. In a series of tables the values are given for thirty-two samples of acid of the specific resistance in true ohms at temperatures of 0°, 15°, and 30°, the temperature coefficients α_{10° and β_{10° deduced from the equation $R_t = R_0(1 + \alpha t - \beta t^2)$, as also for $K_0 \times 10^8$, $K_{15} \times 10^8$, and $K_{30} \times 10^8$ (the conductivity of mercury at 0 being taken as unity, and its specific resistance as 94.07 microhms per l c.c.).

It is shown that the specific resistance decreases for percentage concentrations from 1.30 to 30, at first more, then less rapidly (thus confirming the previous observations of Kohlrausch); from this point the resistance increases slowly up to 76 per cent., thence more rapidly until a maximum is reached at 96.12 per cent., when a sudden reversal takes place.

Further, whereas nitric acid behaves as other electrolytes in possessing a positive temperature coefficient of conductivity for percentage concentrations from 1.3 to 96.12, yet from this point up to

99.97 per cent. it behaves as a metallic conductor in possessing a negative temperature coefficient.

Similar phenomena have been observed by Arrhenius in the cases of moderately dilute solutions of hypophosphorous and phosphoric acids, and explained by him by means of the ionic dissociation hypothesis. It is pointed out that nitric acid of 96—99.97 per cent. would *ex hypothesi* contain few, if any, free ions, and therefore the theory would lead to a totally opposite conclusion.

The results of the experiments are also discussed in relation to the hydrate theory of solution, and the illustrative curves in which the percentages of acid are taken as abscissæ and the resistances or conductivities in mercury units show points of discontinuity markedly at percentages corresponding approximately to the composition required for the hydrates $\text{HNO}_3, 2\text{H}_2\text{O}$, $\text{HNO}_3, \text{H}_2\text{O}$, $2\text{HNO}_3, \text{H}_2\text{O}$ ($= \text{H}_4\text{N}_2\text{O}_7$), and less markedly for the hydrate $\text{HNO}_3, 10\text{H}_2\text{O}$. Further, if the values of $\alpha \times 10^4$ and $\beta \times 10^6$ are referred to molecular proportions of water, the minima values of the former and the maxima of the latter occur in the cases of 3.07, 1.84, 0.99, and 0.55 molecular proportions or very approximately $\text{HNO}_3, 3\text{H}_2\text{O}$, $\text{HNO}_3, 2\text{H}_2\text{O}$, $\text{HNO}_3, \text{H}_2\text{O}$, and $2\text{HNO}_3, \text{H}_2\text{O}$. Further evidence is thus added by an independent method to that already accumulated as to the existence of definite combination of nitric acid with water. Finally, it is pointed out that if a curve is plotted out in which the molecular proportions of water are taken as abscissæ and the values for $\alpha 10^4$ as ordinates, there are ascending and descending branches, meeting at the points corresponding to the formation of the respective hydrates; the phenomena are compared with those observed by Bakhuis-Roozeboom for the solubility curves of hydrates of ferric chloride and by Le Châtelier, as also by Heycock and Neville for the freezing point of alloys.

“On the Refractivities of Air, Oxygen, Nitrogen, Argon, Hydrogen, and Helium.” By Professor WILLIAM RAMSAY, Ph.D., LL.D., Sc.D., F.R.S., and MORRIS W. TRAVERS, B.Sc. Received November 18,—Read December 9, 1897.

In the course of a research on the nature of helium many measurements of its refractivity referred to that of air as unity were made by means of an apparatus similar to that described by Lord Rayleigh.* Inasmuch as the refractivity of helium is very small it was not found convenient to measure its value directly against air; hence it was compared with hydrogen, and hydrogen was compared with air.

* ‘Proceedings,’ vol. 59, p. 203.